

DROSSING OF ZINC IN GALVANIZING PANS

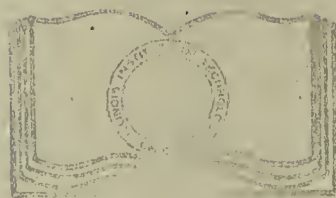
BY

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The dropping of zinc in
galvanizing pans



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THE DROSSING OF ZINC
IN
GALVANIZING PANS

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This investigation was carried out at the plant of the Gilbert & Bennett Mfg. Co., at Wireton, near Blue Island, Ill., and in the Nassau Plant Laboratory as a result of a complaint made by Gilbert & Bennett that the Nassau Spelter which had been furnished to them by the Mineral Point Zinc Co., was producing excessive quantities of dross. It was claimed that up to the middle of September, no trouble had been experienced. The dross produced averaged about 10% of the spelter used which was a Normal quantity in good galvanizing practice. Since that time, the quantity of dross has been excessive, running as high as 17% during one week, and averaging about 13%. As far as they could say there had been no change in the conditions at the plant and they therefore thought that the spelter must have been defective. No analyses had been made nor did they have any evidence that the spelter was of inferior quality. Neither had they made any specification in their orders that the spelter supplied should be of any particular quality. In fact they did not know what quality they did require.

One of the writers of this report was therefore

stationed at the Gilbert & Bennett plant to observe methods and conditions and to take samples to serve as a basis for a thorough study on the problem, both from a practical and from a theoretical standpoint.

THE NATURE OF DROSS

Dross is the material which accumulates in the bottom of the pan containing the bath of molten zinc, through which iron or steel sheets or wire are passed in the process of hot galvanizing. It is a semi fluid, somewhat granular material, of a "Mush like" consistency. It is removed from the pan from time to time (in the present case, at the end of each shift) by means of a heavy shovel, profusely perforated with holes, about 0.5" in diameter., A quantity of the dross, more or less mixed with free Zinc is brought to the surface of the bath on this shovel. The mass is vigorously stirred with iron rods, permitting the greater part of the free Zinc to run through the holes in the shovel and fall back into the bath. The concentrated dross is then dumped into an iron mold. By the time it reaches the mold it has cooled to such an extent that it will not

flow freely and a heavy iron tamper is used to force it together.

If a specimen of dross is ground to a plane surface, polished, then etched with dilute hydrochloric acid and examined under a microscope, it is seen to consist of a mass of small crystals mixed with enough free Zinc to give it its semi fluid consistency when heated above the melting point of Zinc. The appearance of these drosses under the Microscope is shown in the photographs. Nos. 37, - 298, & 453,- which were made from samples of dross taken from the pans at the Gilbert & Bennett plant. The white angular areas are the crystals which have separated out from the matrix of spelter which makes up the dark surrounding areas. No. 462 is a dross prepared in the laboratory with very slow cooling to permit the formation of large, clearly defined crystals. Similar coarse grained structure is obtained when any of the drosses are cooled very slowly.

Chemical analysis shows that the drosses made at the Gilbert & Bennett plant carry 3% to

4.5% of iron, the rest being zinc with whatever other constituents are present in the spelter used. The percentages of these other constituents in the dross are about one-half of those found in the original spelter. For example, during the first part of the test, a spelter was used, having the following analysis of constituents other than zinc.

Iron	0.021%
Lead	0.83%
Cadmium	0.23%

A dross obtained during this time carried

Iron	3.59%
Lead	0.43%
Cadmium	0.11%

This fact is very easily explained by the following consideration:

The microscopic examination shows that in a dross of this composition the relative quantities of crystals of "pure dross" and of the matrix of spelter are about half and half. The crystals consist of a compound of iron and zinc, in the proportions of about 7% iron and 93% zinc. If these crystals, in separating from the zinc, take up none of the other constituents present in the spelter, the quantities of these other constituents in the dross will be only what

are contained in the matrix of spelter surrounding the crystals. Since this matrix makes up about half of the mass, the percentage of lead and cadmium in the entire dross will be about half of those found in the spelter. This is the case in the example cited.

The fact that this relation does hold is an indication that the lead and cadmium in the spelter have no effect on dross formation.

THEORETICAL CONSIDERATIONS.

A case like this, involving the separation of a crystalline substance from a melted mass forms an excellent example of heterogeneous equilibrium. It is beyond the scope of this report to go into an extended discussion of the subject, but it may be stated briefly that such a separation is the necessary consequence when certain conditions of temperature and concentration prevail. (The term concentration, in this connection means the relative proportions of the different constituents in the molten mass.) These conditions are absolutely fixed for any substance or mixture of substances, and any alteration in the concentration or temperature beyond certain definite limits will always produce the same results at the same temperatures and concentrations.

For example, given a quantity of Molten Zinc at a temperature of 500°C . If iron is added, the Zinc will absorb it, forming a solution of iron in Zinc. When the quantity of iron added has increased until it forms

about 0.8% of the total mixture, the Zinc becomes saturated, i.e. it can hold no more iron in solution. If now, more iron is added in suitable form, it is not dissolved by the Zinc as before but forms a compound of iron and Zinc which immediately crystallized out forming dross. The solution of iron in Zinc still remains of the same concentration, a saturated solution, but is decreased in quantity, as some of the Zinc was removed to combine with the excess of iron.

Similarly, given a Molten mixture of Zinc and iron, containing 0.8% of iron, at any temperature above 500°C this system will be entirely liquid. If the mixture is cooled to 500° the same condition of saturation obtains as in the first case cited. If the cooling is continued, so that the temperature is below 500° there is again a precipitation of dross crystals. Both of these effects are reversible, that is, if the opposite change in conditions is made the opposite effect invariably results.

In the first case, if iron is extracted from the mixture of dross and iron-in-zinc solution, the crystals are absorbed and a homogeneous fluid mass results. This is the case in the Richards process for refining dross in which the dross is heated with sulphur and other materials. The sulphur combines with the iron, removing it from combinations with the Zinc, until the concentration of the iron in the mass is below saturation, where upon the entire mass melts.

In the second case, if the temperature of the mixture is raised to above 500° the crystals which had formed on cooling are again melted and a homogeneous melt results.

This system, iron-zinc, has been very thoroughly studied by a number of authorities who have determined the equilibrium conditions for all temperatures and concentrations. A bibliography of the more important articles on the subject is given at the end of this report, also a copy of the equilibrium diagram as given

by Vegesack in the Zeitschrift für anorganische Chemie, Vol 52 (1907) page 37 and reprinted in the Landolt-Bernstein-Roth Physikalisch Chemische Tabellen, 4th edition (1912) page 680. This diagram covers all concentrations up to 22% iron, at temperatures up to 800° C., both of which limits are far beyond any conditions found in galvanizing. The curved line shows graphically the temperature and concentrations at which the separation of crystals begins. Any system whose temperature and concentration are represented by a point above or to the left of this line is in the liquid field, i. e. it is completely liquid. Any point to the right of, or below the line represents a system containing separated crystals of one or more compounds of iron and Zinc.

It is thus seen that dross formation will result, even from absolutely pure Zinc if iron is added in excess of certain definite proportions, the exact proportions depending on the temperature. The only question that arises in

the case of Gilbert and Bennett's complaint is whether the other constituents, such as lead, cadmium, etc., might not so alter the equilibrium as to cause dross to separate at higher temperatures or at lower iron concentrations than are found in the case of the pure metals.

To settle this point definitely it is only necessary to determine the crystallization points of drosses obtained from the galvanizing pans which were giving the trouble. Two such determinations were made one with a dross taken from the south pan at the Gilbert & Bennett works when a high percentage of dross was being made, the other with a portion of the same dross mixed with a portion of the liquid spelter taken from the upper part of the same pan at the same time. This was in order to reduce the iron concentration and thus check two distinct points on the curve.

These determinations were made by the cooling curve method. The sample was melted in an Acheson Graphite Crucible in an electric

furnace, the surface of the sample being protected from oxidation by a layer of powdered charcoal. Temperatures were observed with a platinum, platinum-rhodium thermo-couple and a Siemens and Halske, d'Arsonval type high resistance Millivoltmeter. The couple was protected by quartz tubes. It was carefully calibrated for the range of temperatures of the experiments by checking against the known freezing points of pure zinc and pure aluminum. Cold junctions were kept during calibration and determinations on drosses at 0°C. by enclosing them in thin walled glass tubes immersed in snow.

In making a determination, the sample was first heated to a temperature well above the crystallization point, the current cut off from the furnace and the melt allowed to cool slowly. The temperature was taken at 15 second intervals, and the results plotted in the usual manner. The commencement of crystallization was indicated by a sharp break in the curve. A second break came at the point

where the whole mass crystallized completely. To see if there was any tendency toward undercooling one of the samples was run first as described, then remelted and cooled again while being vigorously stirred. The same crystallization points were obtained in both cases, indicating that there was no undercooling in the case of the unstirred one. When the sample was cold it was cleaned from adhering carbon, oxide, etc., and cut up with a hack saw, the saw dust being collected for analysis.

Sample #447 - Straight dross

Iron - 3.7%

Crystallization temperature- 659° C.

Sample #460- Same dross plus excess of spelter

Iron - 2.1%

Crystallization temperature- 621° C.

Both of these points fall exactly on the curve as found for the pure zinc-iron system by von Vegesack, whose results have been checked by other competent observers- (see papers by Guertler and Raydt & Tamman, mentioned in the

bibliography) This shows that the other constituents present in this spelter did not shift the equilibrium to an appreciable extent, and proves beyond question that the spelter of which Gilbert and Bennett complained was not the cause of their excessive drossing.

One point that might cause some uncertainty as to the soundness of this conclusion is the fact that samples taken from the upper part of the melted bath invariably showed less iron than is required by theory for a saturated solution. This was satisfactorily cleared up by the following experiment.

A sample was taken from near the surface of a pan in which there was a considerable accumulation of dross. The temperature of the bath at this time was 515°C , and analysis showed 0.13% iron - For this temperature, theory requires 0.9% iron before crystallization or dross formation can start. A polished and etched section of this sample shows, under the microscope numerous small dross crystals scattered throughout the mass. (See photomicrograph #242)

A portion of this sample was then remelted and held at 500° for about an hour, then poured into a mold and a section cut and polished. The result is shown in photomicrograph #242 R. Every trace of the dross crystals has disappeared, showing that they were completely absorbed by the Zinc. In other words the system shown in #242 was not in equilibrium.

The explanation is simple. When the iron wire is run through the bath, a condition is super-saturation results in a small region immediately surrounding the wire. Dross crystals are formed and immediately settle toward the bottom of the pan. As soon as they leave the region in direct proximity to the wire, they are in a region where the spelter is unsaturated with iron. If given sufficient time they would redissolve as did the crystals in the remelted sample, thus increasing the concentration of iron in the melt. Owing to their rapidity of settling and comparatively slow rate of solution, there is not sufficient time for this and the crystals settle to the bottom

of the pan where a true, stable equilibrium exists, the crystals being surrounded by a saturated melt. Diffusion into the upper regions is prevented by the mass of solid crystals and by the fact that the lower parts of the bath are not stirred in any way. At the same time the concentration of iron in the upper layer is kept down by the addition of fresh spelter four times a day.

OBSERVATIONS AT THE GILBERT & BENNETT PLANT.

This plant is located at Wireton, about a mile west of Blue Island, Illinois, and makes various grades of wire fencing, netting, cloth, etc. Most of this material is galvanized. With some kinds, the wire is galvanized before weaving with othersthe cloth, netting etc., is woven from the bare wire and the woven material then galvanized.

For this galvanizing, four pans are in use. Two small ones handle the straight wire before weaving, the other two, larger ones, the woven material. It is in these larger pans that the trouble, on which the complaint was based, was experienced. The pans are trough shaped, about 8.5 ft. long 3 ft. wide and 18 in. deep, of semi-circular cross section and built of heavy steel plate. These are mounted in brick settings with fire boxes for coal firing under the entire length and flues for the hot fire gases along both sides.

A brief description of the method used follows:

The netting is brought to the galvanizing room in rolls of 600 ft. each. For each run different widths are selected such that the total width will nearly fill the total length of the pan. Some times a double run is made, two sets being run through simultaneously. The rolls are first immersed in a tank of hydrochloric acid to remove rust and scale. Two of these acid tanks are provided for each pan. The acid in these tanks is practically never changed except to replace, from time to time, by the addition of fresh acid, the loss of acid carried out on the rolls of wire when they are removed. About one carboy per day of commercial Muriatic Acid is added to each tank. More acid is required to replace the loss when running wire cloth than when running netting, as is to be expected, on account of the more numerous points where the wires cross, and which retain large drops of the acid.

When the preceding run is finished, the rolls are lifted out of the acid and hung on a

length of pipe, run through the middle of the rolls, and suspended on hooks on a frame beside the galvanizing pan. Wires are ran through the bath from the opposite side, hooked on to the ends of the netting and the other ends attached to a reel driven by power. When all is ready the reel is started and the netting or cloth is drawn through the Molten Zinc, passing under two rollers carried by a partition which divides the pan in two lengthwise. The partition dips about two inches below the surface, and the rollers are so held that the wire runs about four inches below the surface, of the bath. These rollers are adjustable and the depth of immersion may be varried if necessary,

On the exit side of the partition, the bath is covered with a layer of soft coal screenings about six inches in depth which is kept moist with a solution of bleaching powder. This serves as a wipe, to remove excess zinc and brighten the coating.

The wire is drawn through at the rate of about 30 feet per minute.

As soon as one run is started through the pan the rolls of bare wire for the next run are dropped into the acid tanks where they are allowed to remain until time for the next run.

At the beginning of this test, one of the pans (the North pan) was completely cleaned out, in order to start with new spelter of known quality and source. For this purpose a car load of selected spelter was shipped from Nassau. This was Lot #6301, made October 7 to 9, 1914 in Furnaces #1 and #7 from Wisconsin Separator Ore.

Analysis of this lot showed:

Iron	0.021%
Lead	0.83%
Cadmium	0.23%

The clean pan was filled with 166 slabs of this metal and on November 18th the fire was started at 7 A.M. The entire mass of spelter was melted at about 2 P.M. including 8 additional slabs added when fusion was nearly complete. This made a total of 174 slabs, or about 9750 pounds.

No galvanizing was done on that day, nor during the following night.

On November 19th, galvanizing started at 7 A.M. and at the same time, regular observations were commenced. Temperatures of the bath were taken hourly by means of a Bristol pyrometer, which had been carefully calibrated for this run by taking the freezing points of lead (327°C) Zinc (419°C), and aluminum (658°) and the boiling point of sulphur (445°). In all cases, correction was made for variation of the cold junction temperature from that of standardization.

Samples were taken of the new spelter added, of the melted metal in the pan, and of the dross drawn at the end of each shift. The new spelter was sampled by drilling several slabs each day from the metal to be added the following day. Two kinds of samples were taken of the metal in the bath. One granulated sample for chemical analysis was taken by pouring from a small ladle into a clean bucket of water. The other sample, taken at the same time was prepared

by casting a small stick of the metal by pouring from the ladle into an iron mold. This was for the microscopic examination. Two samples were also taken of each batch of dross, one by drilling the slabs made, the other by filling the mold while the dross was being taken from the pan.

Analysis for iron was made immediately on each analytical sample. Duplicate portions of the analytical samples and all metallographic samples were then mailed to Nassau for further examination.

Record was also kept for a time of the quantity and kind of material galvanized, with the idea that a knowledge of the quantity of wire or its surface area exposed to the zinc might be of value. It soon became apparent however that, with such diverse widths and meshes of material, no definite conclusions could be reached and this part of the record was abandoned.

From the number of slabs added each day the weight of spelter used was calculated, using an

average figure of 56 pounds per slab. The dross made each shift was weighed and the weight recorded.

The results of these observations were plotted as shown on the accompanying log sheets.

During the first five days no dross was drawn. Some was being produced, however, as it could be felt when an iron rod was run down to the bottom of the pan. Photomicrograph #5 shows a sample taken from near the surface of the pan about three hours after galvanizing was started. This shows a few small isolated crystals of dross, sufficient to prove that dross formation starts as soon as galvanizing starts, without waiting for complete saturation of the entire bath with iron. This is in agreement with the theory previously stated.

The first dross was drawn on November 23rd, but owing to too low temperature at the time of drawing it was incompletely separated from excess zinc and was returned to the bath. After

that, dross was drawn every day in gradually increasing amounts. The daily fluctuations are of little significance as the total accumulation of dross was never completely removed, on account of the method used in removing it, which allows a considerable quantity of dross to drop back into the pan through the holes in the shovel along with the excess zinc. The trend of the curve is distinctly upward, however, throughout the run. This is somewhat more noticeable in the curve showing per cent of dross in relation to spelter used, since the quantity of spelter used per day fell off considerable, during the latter part of the run, on account of shortage of work.

During all of this time there was a continually increasing accumulation of dross in the pan until, during the last week it filled all the lower part of the pan and extended to within six or eight inches of the top. It could be easily felt by means of an iron rod, it offered considerably more resistance to the passage of

the rod than did the upper layer of zinc comparatively free from crystallization. There was also a distinctly gritty feel as the rod passed through it. The superintendent insisted that this accumulation was not dross, but could offer no explanation of what it was. A sample prepared in the same manner as the dross samples mentioned before showed under the microscope exactly the same structure as the acknowledged real drosses. Photomicrograph #298 shows a section of such a sample taken from a few inches beneath the surface. #299 is a sample from the surface of the bath taken at the same time. Analysis of #298 shows 2.06% iron, while #299 shows but 0.08% iron.

When the north pan was empty at the end of the run, the metal was cast in slabs. A sample was taken from one of these, selected at random from the pile and a section prepared. Its appearance is shown in photomicrograph #453. This also shows the typical dross structure.

On December 11th, the last of Lot #6301 was used. Instead of continuing with the new

lot of selected metal which had been received those in charge of the plant, without consulting the writers, changed to the old metal of which they had complained. This was used during a part of the 11th and all of the 12th. The plant was shut down on the 13th (Sunday). No spelter was added on the 14th., as it had been decided to shut down the North pan, there not being enough work to keep two pans busy.

During these last three days there was an apparent increase in dross production. The writers feel very certain that this increase was apparent rather than real for these reasons.

1. Analysis shows the old spelter to be fully equal to what had been in use previously during the test.

2. The amount of old spelter used during this time was small compared to the amount already in the pan and could not have produced so marked a result in so short a time.

3. The entire working force seemed bent on supporting the contention that the old spelter was bad. With the large reserve accumulation

of dross in the pan, it was an easy matter to increase an amount drawn when the occasion seemed to require it.

4. On the last day, when no spelter whatever was added, more dross was drawn than on any day previously.

5. Recalculation of the draws from the last five days to give a uniform increase, and the same total production gives the curve shown by the dotted line in the log. This is an accurate continuation of the preceding part of the curve.

It is to be regretted that it was necessary to shut down this pan just at a time, when the dross production had risen to the permissible maximum. The writers believe that had it been continued with selected metal, the dross production would have continued to increase at the same general rate as had prevailed until conditions were about the same as in the south pan in which old metal had been continuously in use. They also believe that if the run had been continued with the old metal, the first

sudden increase would have been followed by a gradual decrease until the final result would have been the same. The reasons for this belief will appear in the discussion of the run on the south pan.

No definite conclusions can be drawn from the record of temperatures. An accident to the pyrometer put it out of commission for several days, early in the test, indicated by a dotted line in the log. It is noticeable that the temperature was somewhat higher during the latter part of the run while more dross was being drawn than during the first part. The Gilbert & Bennett people claim that higher temperature produces more dross than low temperature. If this is true it must be due to more rapid absorption of iron by the zinc at high temperatures. It may on the other hand, be a confusion of cause and effect, resulting from the necessity of increasing the temperature when there is a large accumulation of dross in order to keep the metal fluid.

On December 1st., observations were also started on the south pan and carried on

simultaneously with those at the North pan. These are shown in the second log sheet. Up to the time when the north pan was shut down, on Dec. 14th, old spelter was in use. Temperatures were rather high, averaging considerably over 500° C. and dross formation was high, averaging 13.4% of the spelter used. On Dec. 14th, they changed to two net lots of selected spelter. These were Lots #6227 shipped from Nassau November 25th, and Lot #6203 shipped December 5th. Analysis of Lot #6227 showed:

Iron	0.014%
Lead	0.80%

Analysis of Lot #6203

Iron	0.019%
Lead	0.78%

Operation was continued for two weeks with no marked change from the change in spelter. The temperature averaged about the same as during the previous two weeks and the dross production was still high, but somewhat lower, averaging 12.4% of the spelter used.

During the period from December 1st to December 26th. half of which time was on old spelter and half on new, the dross had averaged 13% of the spelter used. The daily consumption of spelter was 4160 lbs. and the daily production of dross averaged 543 lbs. The spelter averaged 0.025% iron or a total of 1.04 lbs. of iron introduced into the bath by the spelter each day. The dross drawn averaged about 3.2% iron corresponding to 17.9 lbs. of iron removed from the bath each day in the dross. The difference, or 16.9 lbs. was derived from some source other than the spelter and was the real cause of the excessive drossing.

There are but three possible sources for this excess iron.

1. The pan itself. - - This being of steel plate is attacked by the molten zinc to a limited extent, but not to such an extent as to supply more than a very small part of the iron necessary for the dross formation. A

pan in constant use lasts for six months to a year, and then fails from local perforation, not from a general weakening all over the surface.

2. The wire being galvanized. - - This undoubtedly furnishes some iron, probably more than the pan since it is not protected by oxide. But it does not furnish all, nor even a major part of that appearing in the dross. Absorption of iron from the wire must be proportional to the surface area of the wire in contact with the zinc. All of the products galvanized at this plant are of about the same sizes of wire, so that in a given weight of netting there is approximately the same area of wire surface as in the same weight of wire cloth. But, the quantity of spelter used in galvanizing a given weight of cloth is about 2.5 times that used on the same weight of netting. With the same surface of wire exposed, there should then be the same weight of dross produced and the ratio of dross to spelter used should be 2.5 times as

great in the case of netting as in the case of cloth. This is not the case, however, as they find that the percentage of dross to spelter is about the same in both classes of material. This leads inevitably to the conclusion that the iron in the dross is not absorbed from the wire.

3. The pickling acid. - - This is the only other possible source of iron with which the spelter comes in contact, except the tools, scrapers, rods, etc., which are very light and are not visibly attacked even after long use.

As mentioned before, the rolls of woven wire are taken directly from the acid tanks to the galvanizing pan. They are coated with a film of the acid when drawn into the bath. This acid is saturated solution of ferrous chloride. Considerable quantities of the crystallized salts are deposited in the bottoms of the tanks, enough to keep the solution saturated at all temperatures, with the thorough agitation which it constantly receives. The

iron concentration varies with temperature and acidity, but at the time of this investigation, it contained about 8% by weight of iron. It's specific gravity was 1.34 at 23° C. If, as previously stated, about two carboys of acid are used each day in replacing the loss from the tanks at each pan, there is removed on the wire an equal volume of acid. This means that about 290 pounds of acid are carried into the molten zinc each day, including 8% or 23 pounds of iron as Chloride. This is more than sufficient to account for the iron in the dross.

Ordinarily, in aqueous solutions, zinc will not reduce iron compounds below the divalent, or ferrous condition, in which condition it could not alloy with the zinc. In the galvanizing bath, totally different conditions prevail. The water of the acid solution is completely evaporated, leaving the dry solid salt to react on the molten spelter at temperatures around 500°. Nothing was to be

found in the literature as to the reaction under these conditions and the following experiment was carried out to determine whether, under the conditions prevailing in a galvanizing plant, the iron chloride would be completely reduced to metallic iron which could then alloy with the zinc.

A quantity of the pickling acid from the acid tanks at the Gilbert & Bennett plant was evaporated to dryness, yielding its ferrous chloride as the dry salt. This was analysed and enough weighed out to supply 2 grams of iron. 100 grams of Horsehead spelter carrying 0.010% iron were placed in a porcelain crucible in an electric furnace, the spelter melted and brought to a temperature of 500° C at which point it was held constant. The weighed portion of iron chloride was then slowly added to the spelter which was stirred, after each addition, with a quartz rod. In this way, the zinc came in contact with no iron other than that in the chloride. Before the entire portion of iron chloride had been added, the spelter took on the pasty appearance

of dross, becoming quite thick. The furnace was then closed and the current shut off allowing the melt to cool slowly. Photo-Micrograph #462 shows a section of the resulting dross. #463 shows the appearance of a section of the original Horsehead spelter, prepared and etched in exactly the same way. The latter shows no separated crystals whatever, merely a coarsely mottled surface. The other however, is totally different in its appearance - Large, sharply defined, angular crystals, resistant to the action of the etching acid and therefore retaining their polished surface, are prominent. The structure is identical with that of the true dross (#37) but somewhat coarser, on account of slower cooling.

Analysis shows 2.80% iron instead of the 0.01% of iron found in the original spelter. This is somewhat higher than the calculated concentration, but is accounted for by a loss of zinc by volatilization and

oxidation while adding the chloride.

This experiment proved definitely that under the conditions prevailing in the galvanizing plant, zinc does absorb iron from iron chloride and points to the acid solution as the probable source of the bulk of the iron in the dross.

Arrangements were then made with the Gilbert & Bennett people to test out this point. The two acid tanks at the idle North pan were thoroughly cleaned out and one was filled with fresh water, the other with a freshly prepared acid solution made by diluting fresh acid with clean water in equal proportions.

Beginning December 28th, the rolls of wire, after removal from the foul acid solution, were thoroughly rinsed by dipping in the fresh water, then given a dip in the clean acid, as it was necessary to have the wire coated with acid when run into the pan, in order that the zinc should adhere properly.

The results were apparent almost immediately. While the percentage of dross drawn to spelter used was but little affected for several days, it was noted that the workmen, who resented the additional labor involved in washing the wire, were doing all in their power to prevent a reduction in the quantity of dross, in order to prove that the washing was of no use in reducing dross production. In spite of their efforts there was a gradual lowering in the quantity of dross drawn per day. The result of real significance, however, was an immediate reduction of the quantity of the drossy accumulation in the pan. Up to this time, this accumulation was always present in the pan extending from the bottom to within a few inches of the top of the bath, and no attempt was made to reduce it because, as previously mentioned, it was not considered to be dross. In their efforts to keep the dross production up to the previous figures, the men were in reality drawing on this accumulation of dross in addition to the quantity

actually made each day. Another point that is quite apparent from the curves is this: Whereas, previous to starting the washing, there was no marked difference between the day and night shifts in the dross production, the night shift averaging slightly lower in percentage than the day, immediately after the washing was started a radical difference appeared. The production by the night shift rose above any figures that had been obtained at any time during the test, in spite of the fact that the day shift was using every effort to get out all they possibly could. The only conclusion was that, during the night shift, when the Mineral Point Zinc Co.'s representative was not on duty, the washing was being slighted, or omitted altogether. There was no attempt on the part of the Gilbert & Bennett Co. to provide competent supervision of the work, the only foreman being the "head galvanizer" who was supposed to be in charge of the gang, but who was of

the same nationality as the rest and made no attempt to force them to carry out instructions.

Observations on both day and night shifts were started on Monday, January 4th. Dross production by the night shift again came down to figures, comparable with those of the day shift. By this time the accumulation of dross in the pan had been completely cleared out and very little was to be felt in the bottom of the pan after the regular removal of that made during a shift. The metal in the pan was completely liquid and it was possible to run with a much lower temperature than had prevailed previously.

v The improvement was so marked that it was decided to end the investigation on January 9th. (saturday) but on Friday, the 8th a quantity of the old spelter was unearth and it was decided to continue until that was used up.

A very unexpected rise in the quantity of dross drawn is noted on Friday and Saturday, with a return of nearly normal figures

on Monday, the 11th, when the old spelter was used up and observations brought to a close. There was not enough of the old spelter to permit a longer run and a thorough investigation of the reason for the sudden rise in those two days. That it was due to the spelter is highly improbable as but a small quantity was used, as light shifts were run on both days and only half night shifts. Analysis showed the old spelter to be of good quality, analysing:

Iron	0.026%
Lead	0.84%

And metallographic examination showed no structural difference between this and the spelter that had been in use during the run with selected metal. Photomicrograph #448 shows a section of a slab of the old metal from furnace #9, which they claimed gave them the most trouble, while #465 is a section of selected metal from Wisconsin Separator Ore. Both show the coarse zinc crystallization but no separation of dross.

In looking for an explanation of the sudden increase, the writers discovered that a pile of drossy metal which had been drawn from the North pan and stored in the far end of the galvanizing room had been tampered with and a number of slabs had disappeared. No explanation of this could be obtained and it is their firm belief that some one, finally convinced that the local practice was to blame for all the past difficulties, but unwilling to admit it, had attempted to make it appear that the old metal was at fault by changing suddenly back to the old metal and adding enough drossy metal secretly to increase the apparent production of dross without giving an opportunity for a thorough investigation. Several other occurrences were noted, pointing to the same conclusion, and leading to the suspicion that the abnormally high drossing of the night shift during the first week after washing started may not have been entirely due to careless washing. Other proofs were so numerous and so conclusive of the real cause

of the past difficulties that the matter was not pressed.

A recapitulation of the results of the test brings out the following points.

1. - Starting with a clean pan and new metal of undoubtedly good quality, drossing increased gradually until it reached the maximum allowed for good practice. It would probably have increased still more had the run been continued. Not nearly all of the dross made was drawn and reported as dross, as the bulk of the metal taken from the pan at the close of the run was of a drossy character.

2. - Running for two weeks on the south pan, using old metal, dross production was high.

3. - On following this with two weeks on new metal of the same quality as used in (1) above, dross production decreased very little and still remained high.

4. - Using the same metal as during period (3) but washing the highly ferruginous

picking acid from the wire, before galvanizing, reduced the accumulated dross in the pan to practically zero and brought the daily production below normal figures.

The writers feel that these results, together with the theoretical proofs brought out in the laboratory, fully warrant the conclusion stated on the first page of this report.

Nassau Plant Laboratory,

January 26, 1915.

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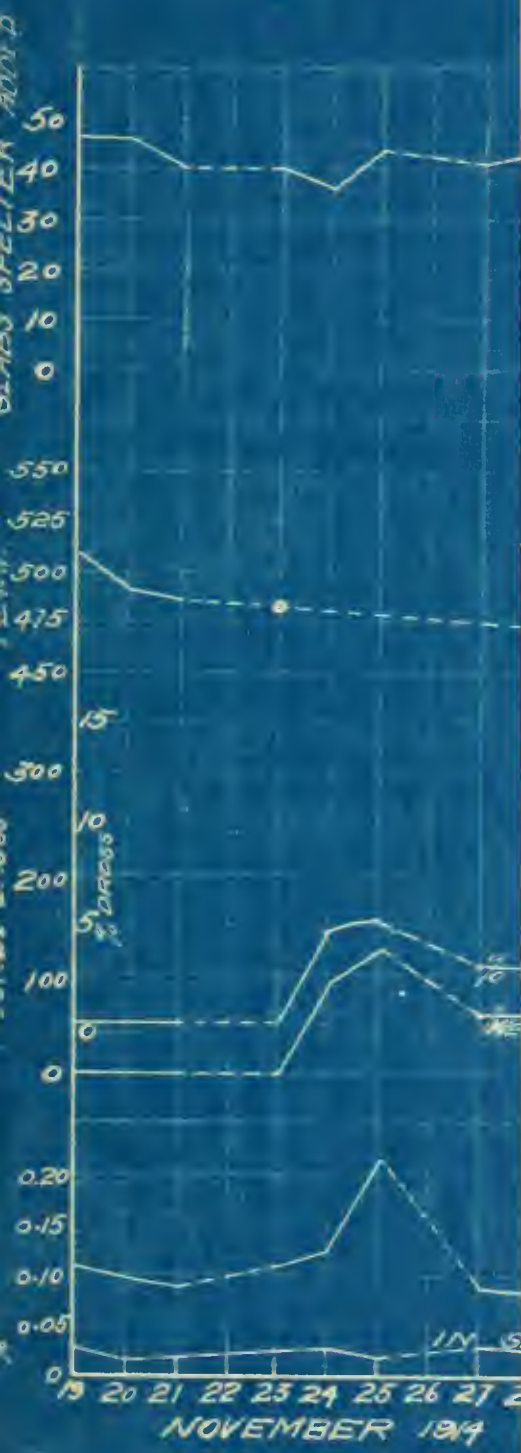
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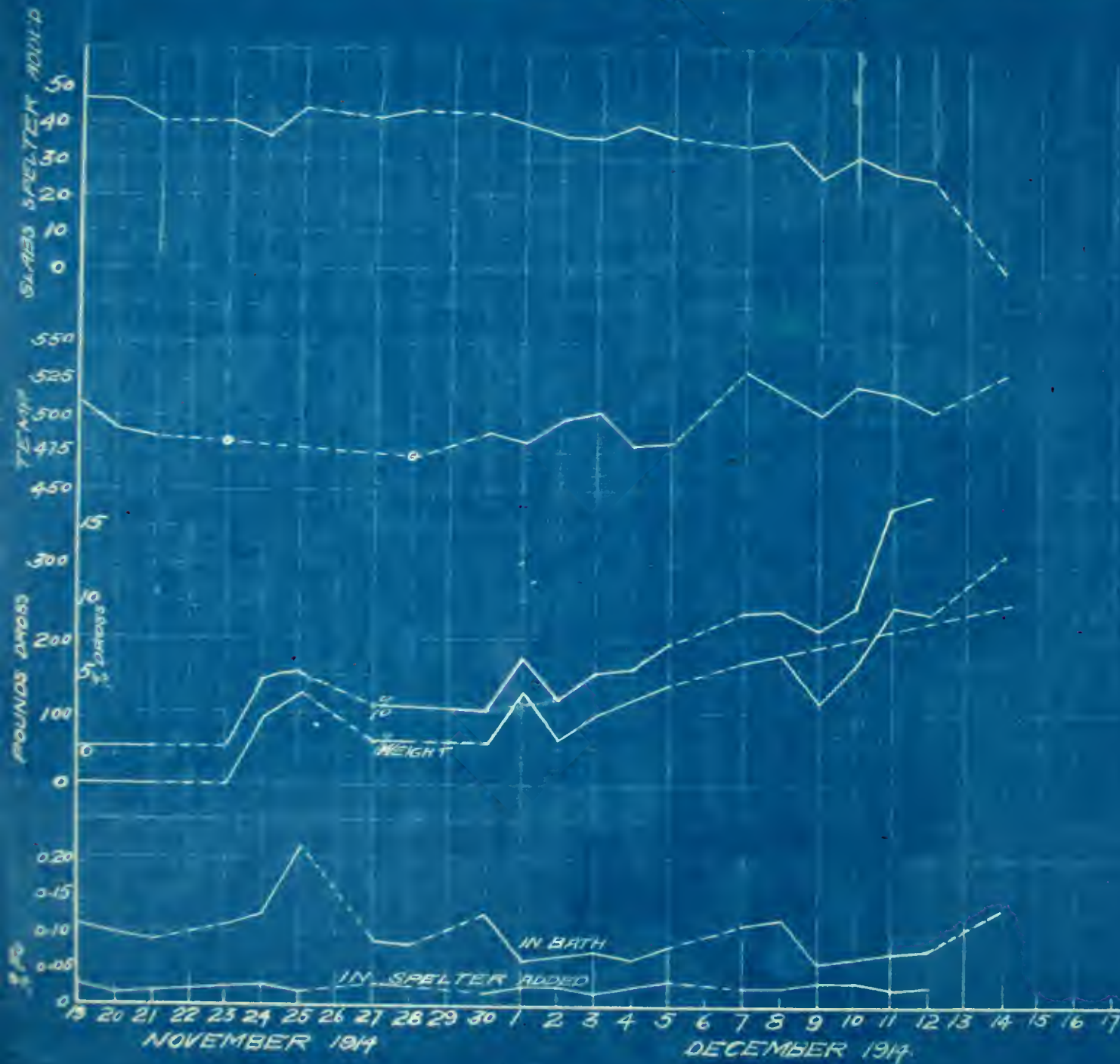
LE CHATELIER

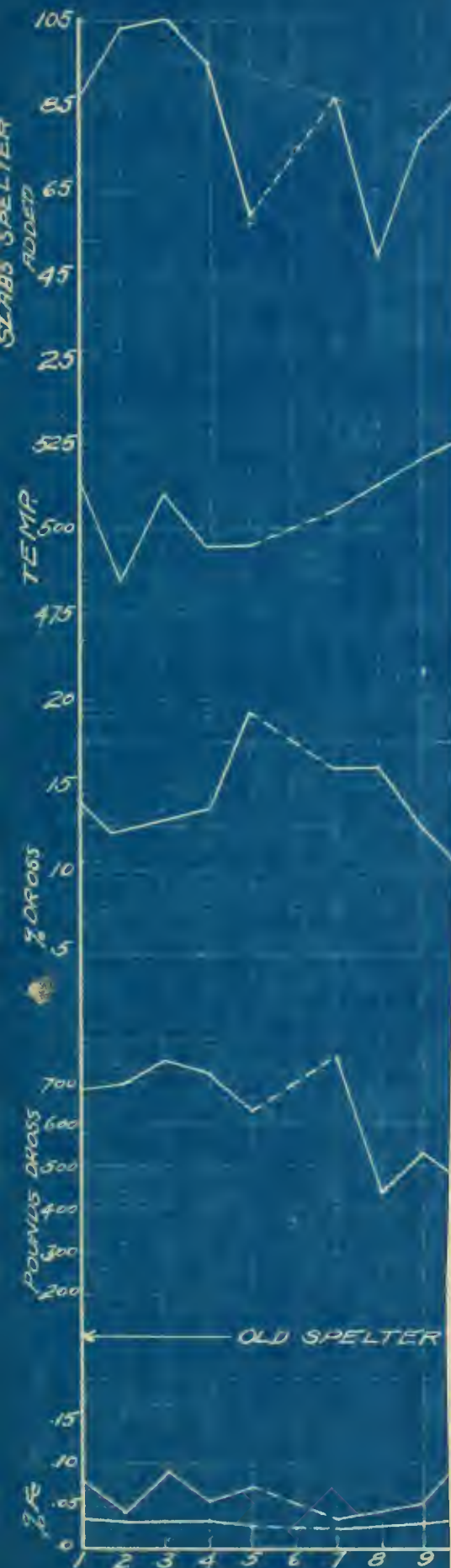
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GALVANIZING TEST
GILBERT AND BENNETT PLANT WIRETON, ILL.
NORTH PAN

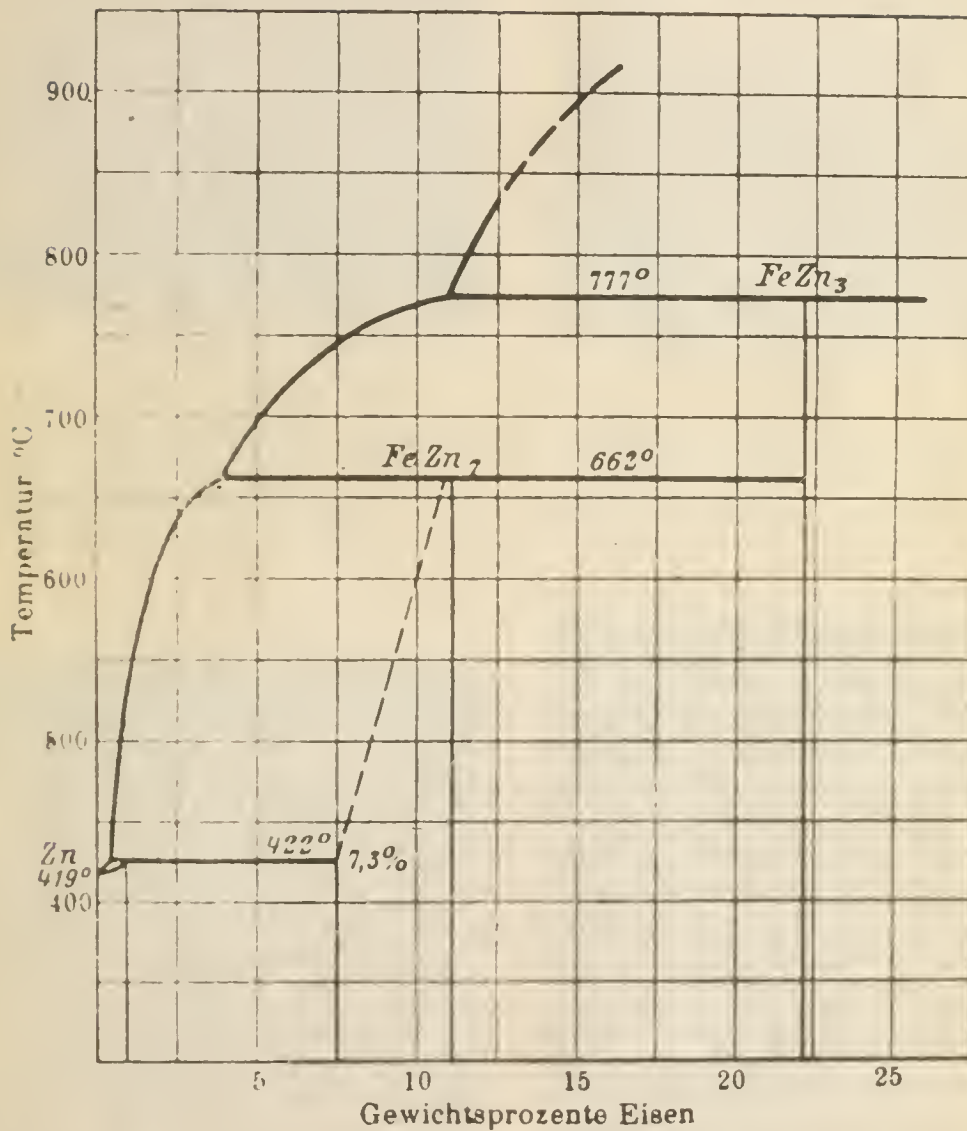




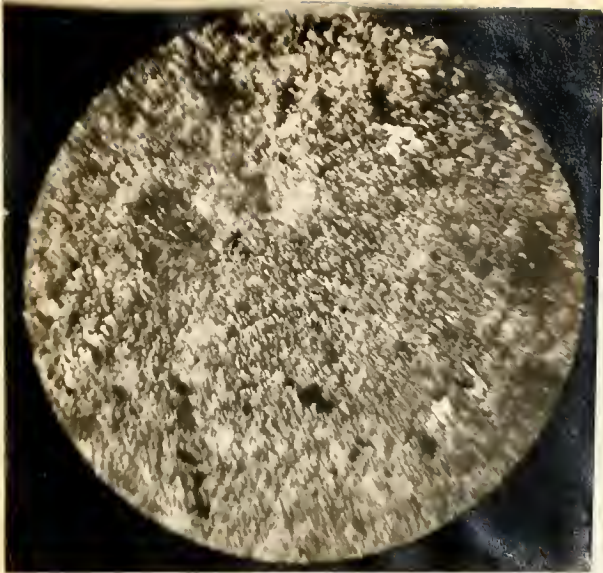
GALVANIZING TEST
GILBERT AND BENNETT PLANT WIRETON, VLL.
SOUTH PAN



172. Fe-Zn Eisen-Zink.

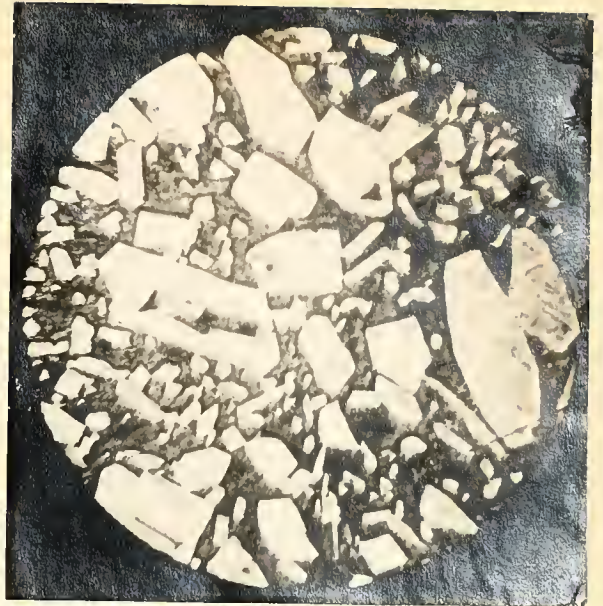


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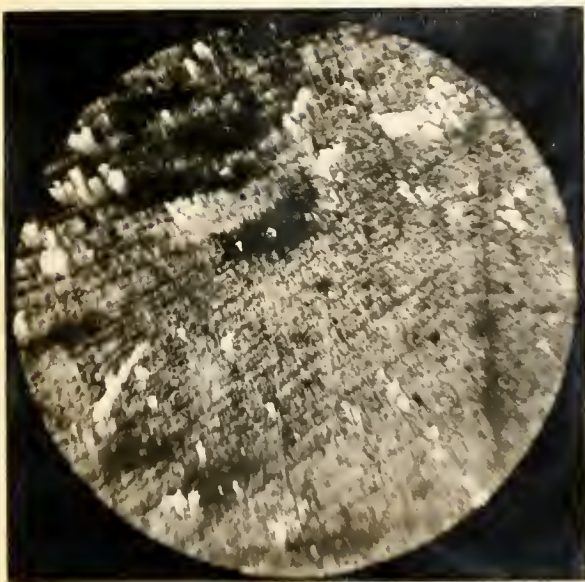
No. 5

Sample from Galvanizing
Pan - 3 hrs. after start-
ing to Galvanize.
Etched with 4% HCl.
Magnification - X 50



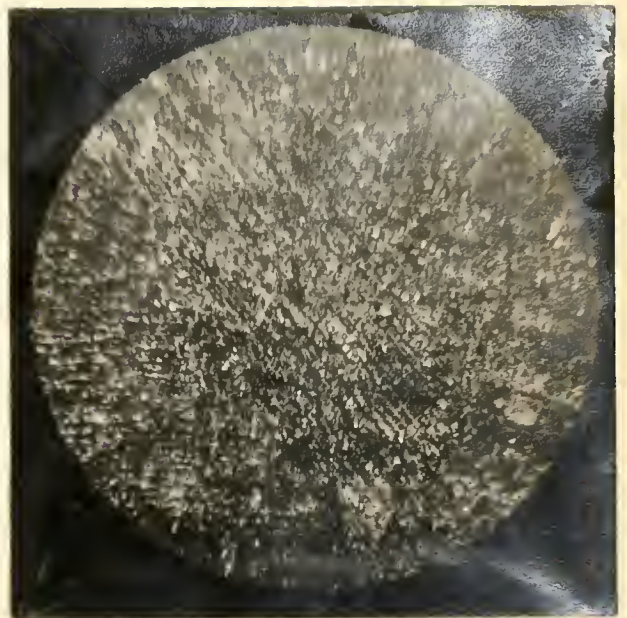
No. 37

Dross drawn from bottom
of pan and separated
from excess zinc. Etched
with 4% HCl X 50.



No. 242

Sample from near surface of
bath. shows dross crystals.
Etched with 4% HCl X 50



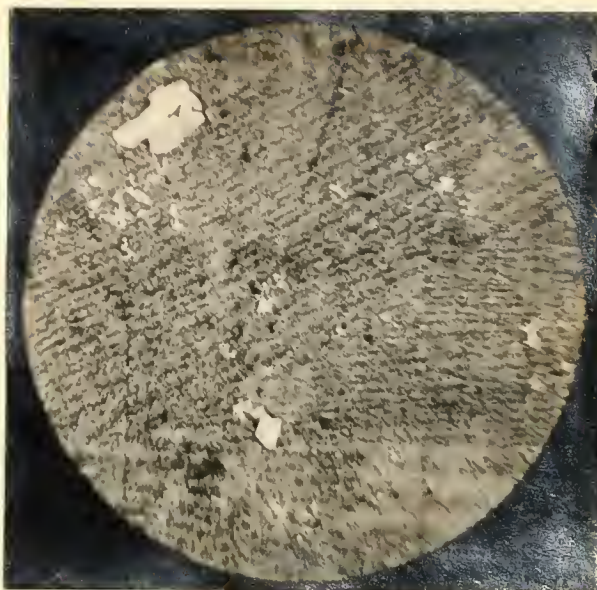
No. 242 Remelted

Same as 242. Remelted and
held at 500°C. shows ab-
sorption of dross crystals.
Etched with 4% HCl X 50



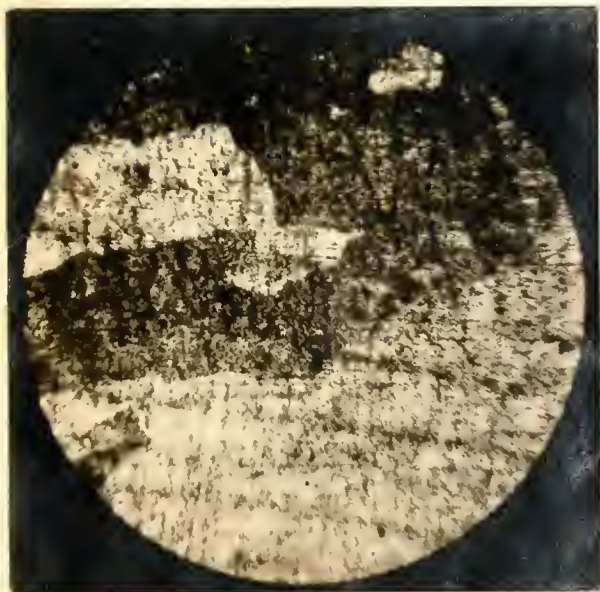
No. 298

Sample taken from Six
inches below surface of
bath. Etched with
4% HCL X 50



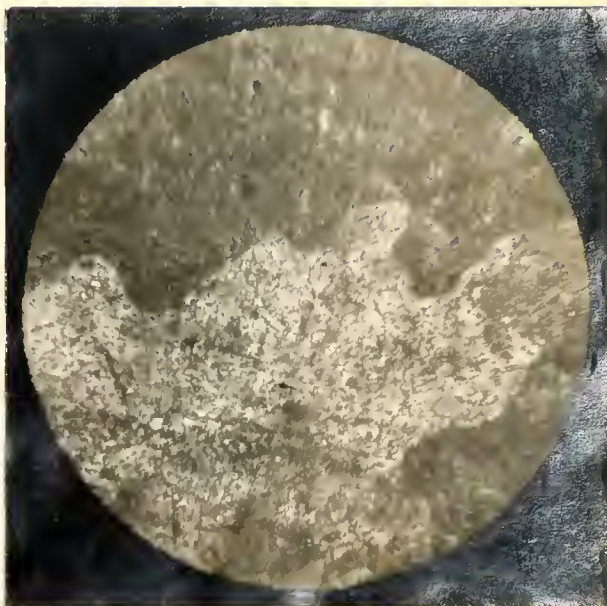
No. 299

Sample taken from Surface
of bath at same time as
298. Etched with 4% HCL
X - 50



No. 448

Sample cut from Slab of
Spelter claimed to be de-
fective, Etched with
4% HCL X 50



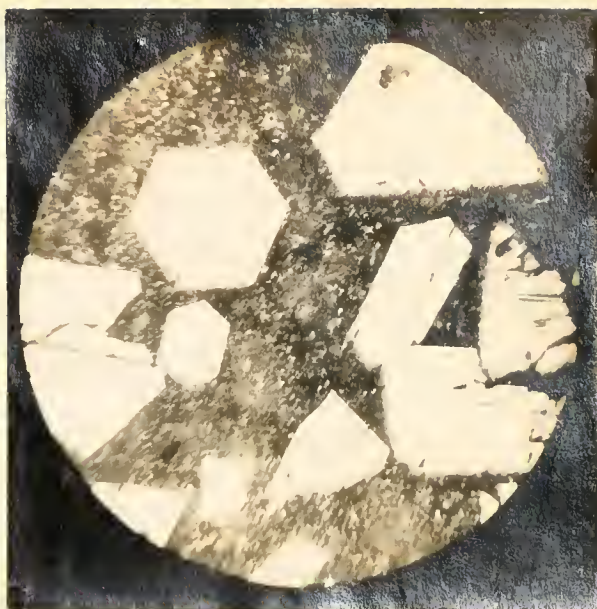
No. 465

Sample cut from slab of
selected Spelter made from
Wis. Sep. Ore. Etched with
4% HCL X 50



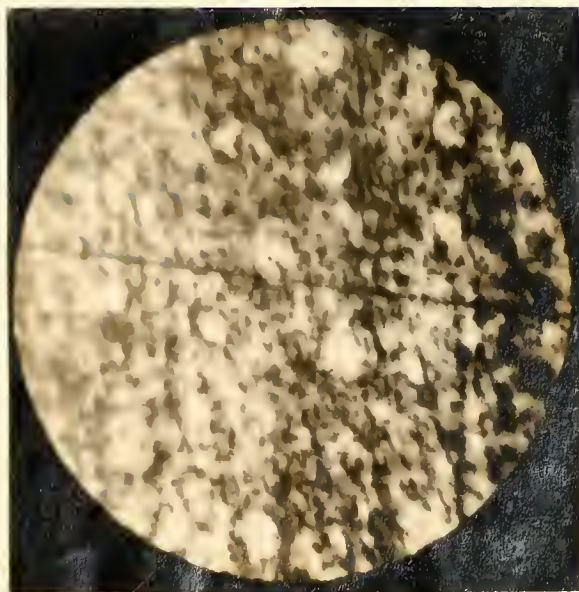
No. 453

Sample cut from Slab of
metal cast when emptying
north pan after test run.
Etched with 4% HCL X50



No. 462

Dross prepared in lab-
oratory from Horsehead
Spelter and Ferrous
Chloride.
Etched with 4% HCl X50



No. 463

Sample of Horsehead
Spelter used in preparing #462
Etched with 4% HCl X50

